Electricity is Different

Bob Eisenberg
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‘Charge’ is an Abstraction with
VERY different Physics in different systems
For me (and maybe few others)

Cezanne’s

Mont Sainte-Victoire*

*one of two at Philadelphia Museum of Art

vu des Lauves

is a

Miracle

*one of two at Philadelphia Museum of Art
See the fraternal twins
(i.e., not identical)

in the

Philadelphia Museum of Art

it is worth a visit,
and see the Barnes as well
Incomparable

Barnes Foundation
Philadelphia
Continuity of Current is a Miracle because

Electricity is Different

It is EXACT and UNIVERSAL

even though

Physics of Current Flow Varies Profoundly
Electricity is Different

Density and Concentration Fields are Weak

One percent change in density does almost nothing

The Electric Field is Strong

One percent change in charge lifts the Earth,
Electricity is Different

The Electric Field is Strong

If you were standing at arm’s length from someone and each of you had

One percent more electrons than protons,

the force would lift the Entire Earth!

Electricity is Different

Maxwell Equations are Universal and Exact

\[ \nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0} \]

What is this? NOT exact NOT universal

\[ \nabla \cdot \mathbf{B} = 0 \]

What is this? NOT exact NOT universal

\[ \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \]

\[ \nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \]

As written by Heaviside, using Gibbs notation

\( \mathbf{E} \) is electric field, \( \mathbf{B} \) is magnetic field

\( \mathbf{J} \) is the current of particles with mass

\( \rho \) is charge density (of all types)

\( \varepsilon_0 \) is the permittivity of a vacuum

\( \mu_0 \) is the permeability of a vacuum

\( (\mu_0 \varepsilon_0)^{-\frac{1}{2}} \) = velocity of light (!)

\( \nabla \times \) is the curl operator

\( \nabla \cdot \) is the divergence operator

Displacement Current Everywhere! Inside atoms
Generalized Current is Conserved

Maxwell Equation

\[ \nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \]

- Vector Identity
  \[ \nabla \cdot \nabla \times \mathbf{B} \equiv 0; \quad \text{so,} \quad \nabla \cdot \left( \mathbf{J} + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \right) = 0 \]

- Conservation law

Generalized Current
EXACT & UNIVERSAL
Maxwell Equation $\nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}$ implies

$\mathbf{J} + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}$ is conserved EXACTLY and UNIVERSALLY
\( \mathbf{J} + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \)

is conserved EXACTLY and UNIVERSALLY

**Technical Comment**

**Description of charge** \( \rho \) is problematic because it exists in so many forms with such complex properties. Universal representation of \( \rho \) does not exist!

**Conservation of current** does NOT depend on the properties of charge.

Conservation of current depends on the existence of \( \mathbf{J} \) but not on its properties. \( \mathbf{J} \) exists if magnetism \( \mathbf{B} \) exists.

**Displacement Current** \( \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \) occurs in vacuum. Atoms and matter are mostly vacuum. Only nuclei of atoms contain mass and they are tiny radius \( 10^{-15} \) m, atom is \( 10^{-10} \) m. Volume of nucleus/volume of atom is about \( 10^{-15} \).
Maxwell Equations are Special

Continuity of Current is Exact and Universal

no matter what carries the current

even though

Physics of Charge Flow
Varies Profoundly
even Creating Plasmas!

‘Charge’ is an Abstraction
with

VERY different Physics
in different systems
When we unplug a computer power supply, we often create sparks, i.e., a plasma, a new kind of current flow.

Mathematics of Continuity in Maxwell equations can create new kind of physics, new kind of charge.

\[ i_d = \frac{\partial E}{\partial t} \]
Physics of Charge Flow
Varies Profoundly

but

Conservation of Current is EXACT and UNIVERSAL
‘Charge’ is an Abstraction with different Physics in different systems

but **Conservation of Current** is **EXACT** and **UNIVERSAL**

*No matter what ‘charge’ carries the current!*

‘Charge’ is an Abstraction with different Physics in different systems

but **Conservation of Current is EXACT and UNIVERSAL**

*No matter what ‘charge’ carries the current!*
Electrodynamics and Ions in Chemistry

Applied Electric Field ZERO

Applied Electric Field NOT ZERO
Law of Mass Action

is how chemists have described chemicals, not flows

\[ \text{A} \xrightarrow{k_f} \text{B} \xleftarrow{k_b} \text{A} \]

\[- \frac{d}{dt} [A] = k_f [A]; \quad - \frac{d}{dt} [B] = k_b [B] \]

\( k \) is constant

\([A]\) means the activity or approximately the concentration of species A, i.e., the number density of A
“... incomplete truths learned on the way may become ingrained and taken as the whole truth....

what is true and what is only sometimes true will become confused.”

Richard Feynman
Law of Mass Action

is about

Conservation of Mass and Matter

*It is not about conservation of charge*

\[
X \xleftrightarrow[k_{xy}]{k_{yx}} Y \xleftrightarrow[k_{yz}]{k_{zy}} Z
\]

\[
J_{xy}^{net} = J_{xy} - J_{yx} = k_{xy} [X] - k_{yx} [Y]
\]

\[
I_{xy} = z_x F k_{xy} [X] - z_y F k_{yx} [Y]
\]

[X] means the concentration, really activity of species Z, i.e., concentration is the number density
\[ X \xleftarrow{k_{xy}} Y \xrightarrow{k_{yz}} Z \]

\[ \frac{d}{dt} x = k_{xy} y - k_{yx} x \]

\[ \frac{d}{dt} y = k_{yz} z - k_{zy} y \]

\[ \frac{d}{dt} z = k_{zx} x - k_{xz} z \]

\[
I_{xy} = z_x F k_{xy} [X] - z_y F k_{yx} [Y] \neq 0
\]

\[
I_{xy} \neq 0
\]

[X] means the concentration, really activity of species Z, i.e., concentration is the number density.
Kirchoff Current Law requires

\[ I_{AB} = I_{DE} \]

under all conditions

ALWAYS \( \pm 10^{-17} \), or so

Kirchoff Current Law and Maxwell Equations are nearly the same thing

Itzykson & Zuber Quantum Field Theory (1990) p. 10
‘Current-in’ does not automatically equal ‘Current-out’ in Rate Models if rate constants are independent and Currents are Uncorrelated.

\[ I_{AB} \neq I_{DE} \]

but Kirchoff Current Law requires

\[ I_{AB} = I_{DE} \]
Correlation between currents is in fact ALWAYS

0.999 999 999 999 999 999 999

because

Continuity of Current is Exact

Electricity is Different

Kirchoff Continuity of Current Law
including displacement current
is another form of Maxwell’s Equations
Engineering is about Signal Flow not chemicals
How can this be?

Chemistry is about Chemicals not signals
Maxwell’s Equations
Kirchoff’s Current Law
compute
Signals
from Conservation of Charge
and
Continuity of Current,
including displacement current
Parameterization is not Possible
under more than one condition

Rate constants chosen at one boundary charge or one potential cannot work for different charges or potentials

Currents in Rate Models are
Independent of Charge and Potential
but
in the real world
Currents depend on Charge and Potential
Cause of Frustration

Biochemical Models are Rarely TRANSFERRABLE
Do Not Fit Data even approximately in more than one solution*

* i.e., in more than one concentration or type of salt, like Na\(^+\)Cl\(^-\) or K\(^+\)Cl

Note: Biology occurs in different solutions from those used in most measurements
Physical Chemists are Frustrated by Real Solutions
All of Biology occurs in Salt Solutions of definite composition and concentration and that matters!

Salt Water is the Liquid of Life
Pure H$_2$O is toxic to cells and molecules!

Salt Water is a Complex Fluid
Main Ions are Hard Spheres, close enough

Sodium Na$^+$  Potassium K$^+$  Calcium Ca$^{2+}$  Chloride Cl$^-$

3 Å
“Sometimes it is necessary to put a veil on the past, For the Sake of the Future”

Henry Clay, the Essential American
p. 375 D.S. & J.T. Heidler
Central Result of Physical Chemistry

Ions
in a solution are a
Highly Compressible Plasma

although the
Solution is Incompressible

Free energy of an ionic solution is mostly determined by the
Number density of the ions.
Density varies from $10^{-11}$ to $10^1$M
in typical biological system of proteins, nucleic acids, and channels.

Learned from Doug Henderson, J.-P. Hansen, Stuart Rice, among others…Thanks!
Electrolytes are Complex Fluids

Treating a Complex Fluid as if it were a Simple Fluid will produce Elusive Results
It is not surprising that **Inconsistent Treatments of ionic solutions** have been so **Unsuccessful** despite more than a century of work by fine scientists and mathematicians.

Werner Kunz:

“It is still a fact that over the last decades, **it was easier to fly to the moon** than to describe the **free energy of even the simplest salt solutions** beyond a concentration of 0.1M or so.”

Kunz, W. "Specific Ion Effects"
World Scientific Singapore, 2009; p 11.
“It is still a fact that over the last decades, it was easier to fly to the moon than to describe the free energy of even the simplest salt solutions beyond a concentration of 0.1M or so.”

The classical text of Robinson and Stokes (not otherwise noted for its emotional content) gives a glimpse of these feelings when it says

“In regard to concentrated solutions, many workers adopt a counsel of despair, confining their interest to concentrations below about 0.02 M, ...”

Good Data
It is difficult to even define in a unique way Properties of One Ion when Everything Interacts with Everything

Tremendous Opportunity for Applied Mathematics
Electrolytes are Complex Fluids

After 690 pages and 2604 references, properties of SINGLE Ions are Elusive* because Every Ion Interacts with Everything

Hünenberger & Reif (2011) “Single-Ion Solvation … Approaches to Elusive* Thermodynamic Quantities”

*’elusive’ is in the authors’ choice in the title but emphasis is added
Ions in Water are the Liquid of Life
They are not ideal solutions

Everything Interacts with Everything

For Modelers and Mathematicians
Tremendous Opportunity for Applied Mathematics because
‘law’ of mass action assumes nothing interacts
Chun Liu’s Energetic Variational Principle
EnVarA
Good Data
Compilations of Specific Ion Effect

1. **>139,175 Data Points** [Sept 2011] on-line
   IVC-SEP Tech Univ of Denmark
   http://www.cere.dtu.dk/Expertise/Data_Bank.aspx

2. Kontogeorgis, G. and G. Folas, 2009:
   Models for Electrolyte Systems. Thermodynamic
   John Wiley & Sons, Ltd. 461-523.

3. Zemaitis, J.F., Jr., D.M. Clark, M. Rafal, and N.C. Scrivner, 1986,
   Handbook of Aqueous Electrolyte Thermodynamics.
   American Institute of Chemical Engineers

4. Pytkowicz, R.M., 1979,
   Boca Raton FL USA: CRC. 288.
Mathematics of Chemistry must deal Naturally with Interactions

‘Law of Mass Action’ assumes nothing interacts

So this is a great opportunity for new mathematics and applications!
Mathematics of Interactions in Complex Fluids

Variational Approach

EnVarA

Conservative

Dissipative

\[ \frac{\delta \hat{E}}{\delta \mathbf{x}} - \frac{1}{2} \frac{\delta \Delta}{\delta \mathbf{u}} = 0 \]

‘Law’ of Mass Action including Interactions

From Bob Eisenberg p. 1-6, in this issue
Shielding is a defining property of Complex Fluids

It is VERY hard to Simulate at Equilibrium and (in my opinion) IMPOSSIBLE to Simulate in nonequilibrium Like Batteries or Nerve Fibers because flows involve Far Field (macroscopic) boundaries
Shielding Dominates Electric Properties of Channels, Proteins, as it does Ionic Solutions

Shielding is ignored in traditional treatments of Ion Channels and of Active Sites of proteins

Rate Constants Depend on Shielding and so
Rate Constants Depend on Concentration and Charge
Main Qualitative Result
Shielding in Gramicidin

Averaged Potential along Axis: Variation with Bath Concentration

Potential (millivolts)

Position along Axis (angstroms)

Hollerbach & Eisenberg
Reconciling Mass Action and Maxwell/Kirchoff will no doubt be a Long Journey.
“... incomplete truths learned on the way may become ingrained and taken as the whole truth……

what is true and what is only sometimes true will become confused.”

Richard Feynman
“Sometimes it is necessary to put a veil on the past, For the Sake of the Future”

Henry Clay, the Essential American  
p. 375 D.S. & J.T. Heidler
“Journey of a thousand miles starts with a single step”

in the right direction,
I beg to add to this Chinese saying
As a Chicago Surgeon put it

You better head in the right direction, if you want to get anywhere
That direction needs to include the **Electric Field** calculated and calibrated, global and local,

if the journey is ever to end,

in my view.
Replacement of “Law of Mass Action” is Feasible for Ionic Solutions using the All Spheres (primitive = implicit solvent model of ionic solutions) and Theory of Complex Fluids
‘Law’ of Mass Action including Interactions

\[ \frac{\delta E}{\delta \mathbf{x}} - \frac{1}{2} \frac{\delta \Delta}{\delta \mathbf{u}} = 0 \]

Variational Approach EnVarA

Conservative Dissipative
Energetic Variational Approach allows accurate computation of Flow and Interactions in Complex Fluids like Liquid Crystals.

Classical theories and Molecular Dynamics have difficulties with flow, interactions, and complex fluids.

Engineering needs Calibrated Theories and Simulations. Engineering Devices almost always use flow.
Energetic Variational Approach  
**EnVarA**

Chun Liu, Rolf Ryham, and Yunkyong Hyon

*Mathematicians and Modelers: two different ‘partial’ variations written in one framework, using a ‘pullback’ of the action integral*

\[
\delta E \quad \begin{array}{c}
\text{Conservative 'Force'} \\
\delta \bar{x}
\end{array} \quad - \quad \frac{1}{2} \frac{\delta \Delta}{\delta \bar{u}} \quad = \quad 0
\]

- **Shorthand for Euler Lagrange process with respect to \( \bar{r} \)**
- **Action Integral, after pullback**
- **Composite Variational Principle**
- **Field Theory of Ionic Solutions**: Liu, Ryham, Hyon, Eisenberg
  - Allows boundary conditions and flow
  - Deals Consistently with Interactions of Components
Dissipation Principle
Conservative Energy dissipates into Friction

Conservative

\[
\frac{d}{dt} \int \left\{ k_B T \sum_{i=n,p} c_i \log c_i + \frac{1}{2} \left( \rho_0 + \sum_{i=n,p} z_i e c_i \right) \phi + \sum_{i,j=n,p} \frac{c_i}{2} \int \tilde{\Psi}_{i,j} c_j d\tilde{y} \right\} d\tilde{x}
\]

Dissipative

\[
= - \int \left\{ \sum_{i=n,p} \frac{D_i c_i}{k_B T} k_B T \frac{\nabla c_i}{c_i} + z_i e \nabla \phi - \sum_{j=n,p} \nabla \int \tilde{\Psi}_{i,j} c_j d\tilde{y} \right\} d\tilde{x}
\]

\[c_i \text{ number density; } k_B T \text{ thermal energy; } D_i \text{ diffusion coefficient; } n \text{ negative; } p \text{ positive; } z_i \text{ valence; } \varepsilon \text{ dielectric constant}\]

Note that

\[
\varepsilon \left[ \nabla \phi \right]^2 = \frac{1}{2} \left( \rho_0 + \sum_{i=n,p} z_i e c_i \right) \phi \quad \text{with suitable boundary conditions}
\]
Energetic Variational Approach

\[ \frac{\delta E}{\delta \dot{x}} - \frac{1}{2} \frac{\delta \Delta}{\delta \dot{u}} = 0 \]

is defined by the Euler Lagrange Process, as I understand the pure math from Craig Evans which gives Equations like PNP

BUT
I leave it to you (all) to argue/discuss with Craig about the purity of the process when two variations are involved
**PNP (Poisson Nernst Planck) for Spheres**

Non-equilibrium variational field theory $\text{EnVarA}$

**Nernst Planck Diffusion Equation**

For number density $c_n$ of negative $n$ ions; positive ions are analogous

$$
\frac{\partial c_n}{\partial t} = \nabla \cdot \left[ D_n \left( \nabla c_n + \frac{c_n}{k_B T} \left( z_n e \nabla \phi - \int \frac{12 \varepsilon_{n,n} (a_n + a_n)^{12} (\vec{x} - \vec{y})}{|\vec{x} - \vec{y}|^{14}} c_n(\vec{y}) d\vec{y} \right) - \int \frac{6 \varepsilon_{n,p} (a_n + a_p)^{12} (\vec{x} - \vec{y})}{|\vec{x} - \vec{y}|^{14}} c_p(\vec{y}) d\vec{y} \right) \right]
$$

**Poisson Equation**

$$
\nabla \cdot (\varepsilon \nabla \phi) = - \left( \rho_0 + \sum_{i=1}^{N} z_i e c_i \right) \quad i = n \text{ or } p
$$

Eisenberg, Hyon, and Liu
Semiconductor \textit{PNP} Equations

For Point Charges

Poisson's Equation

\[- \frac{\varepsilon_0}{A(x)} \frac{d}{dx} \left( \varepsilon(x) A(x) \frac{d \phi}{dx} \right) = e P(x) + e \sum_{i} z_i \rho_i(x) \]

Drift-diffusion & Continuity Equation

\[ \frac{dJ_i}{dx} = 0 \quad -J_i = D_i(x) A(x) \rho_i(x) \frac{d \mu_i}{dx} \]

Chemical Potential \( \mu_i(x) \)

\[ \mu_i(x) = z_i e \phi(x) + kT \ln \left( \frac{\rho_i(x)}{\rho} \right) + \mu_{\text{ex}}(x) \]

Not in Semiconductor

Finite Size Special Chemistry
All we have to do is

Solve them!
with Boundary Conditions

defining
Charge Carriers
ions, holes, quasi-electrons
Geometry
Solution* of PNP Equation

\[ J_k = C_k \left( L \right) \left( \frac{D_k}{\lambda} \right) \text{Prob} \{ R | L \} - C_k \left( R \right) \left( \frac{D_k}{\lambda} \right) \text{Prob} \{ L | R \} \]

*MATHEMATICS*

This solution was actually DERIVED by computing many conditional probability measures explicitly by repeated analytical integrations.

Solution was actually DERIVED with explicit formulae for probability measures from a Doubly Conditioned Stochastic Process involving Analytical Evaluation of Multidimensional Convolution Integrals

All we have to do is
Solve them!

Don’t Despair

Semiconductor Technology has
Already Done That!
Semiconductor Devices

PNP equations describe many robust input output relations

Amplifier
Limiter
Switch
Multiplier
Logarithmic convertor
Exponential convertor

These are SOLUTIONS of PNP for different boundary conditions with ONE SET of CONSTITUTIVE PARAMETERS

PNP of POINTS is TRANSFERRABLE

Analytical should be attempted using techniques of

Weishi Liu University of Kansas
Tai-Chia Lin National Taiwan University & Chun Liu PSU
The End

Any Questions?